

WHAT IS CLAIMED IS:

1. A system for depositing a composite polymer dielectric film on a substrate, the composite polymer dielectric film including a low dielectric constant polymer layer disposed between and chemically bonded to a first silane-containing layer and a second silane-containing layer, the system comprising:
  - a process module including a processing chamber and a monomer delivery system configured to deliver a gas-phase monomer into the processing chamber for deposition of the low dielectric constant polymer layer;
  - 10 a post-treatment module for annealing the composite polymer dielectric film;
  - a silane delivery system configured to deliver a vapor flow containing a silane precursor into the system for forming the first silane-containing layer and the second silane-containing layer; and
- 15 memory and a processor in electrical communication with the process module, the post-treatment module and the silane delivery system, wherein the memory includes instructions stored thereon executable by the processor to deposit the silane precursor on the substrate for a first interval to form the first silane-containing layer, deposit the gas phase monomer on the first adhesion promoter layer for a second interval to form the low dielectric constant polymer layer, and deposit the silane precursor on the low dielectric
- 20 constant polymer layer for a third interval to form the second silane-containing layer.

2. The system of claim 1, wherein the silane delivery system is configured to deliver the silane precursor to a silane deposition module that includes a silane deposition chamber and a free radical-generating energy source, and wherein the instructions are executable by the processor to control an exposure of the silane precursor to energy from the energy source to form free radicals in the silane precursor after depositing the silane precursor on the substrate for the first interval.

3. The system of claim 2, wherein the free-radical generating energy source is a UV light source.

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4. The system of claim 2, wherein the free-radical generating energy source is a thermal energy source.

5. The system of claim 2, wherein the free-radical generating energy source is a plasma source.

6. The system of claim 1, wherein the silane delivery system is configured to deliver the silane precursor to the process module.

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7. The system of claim 1, wherein the silane delivery system is configured to deliver the silane precursor to the post-treatment module.

8. The system of claim 1, wherein the post-treatment module includes a heater for heating the substrate, and wherein the instructions are executable by the processor to anneal the composite dielectric layer in a presence of hydrogen in the post-treatment module via the heater after depositing the silane precursor on the low dielectric constant 5 polymer layer for the third interval.

9. The system of claim 8, wherein the heater is a hot plate.

10. The system of claim 8, wherein the instructions are executable by the 10 processor to anneal the composite dielectric layer in a presence of 3-10% H<sub>2</sub> in He.

11. The system of claim 8, wherein the instructions are executable to anneal the composite dielectric layer at a temperature of between approximately 250 and 450 degrees Celsius.

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12. The system of claim 8, wherein the instructions are executable to anneal the composite dielectric layer for a duration of between approximately 2 and 10 minutes.

13. The system of claim 1, wherein the process module includes a cooled substrate holder, and wherein the instructions are executable to hold the substrate at a temperature below the crystallization temperature of low dielectric constant polymer layer while depositing the gas phase monomer.

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14. The system of claim 13, wherein the instructions are executable to hold the substrate at a temperature of between approximately -25 and -55 degrees Celsius while depositing the gas phase monomer.

10 15. The system of claim 13, wherein the cooled substrate holder is an electrostatic chuck.

16. The system of claim 15, the chuck having a surface, wherein up to 10 psi of helium is disposed between the substrate and the surface of the chuck during substrate 15 cooling to aid in cooling the substrate.

17. The system of claim 1, wherein the instructions are executable to hold the substrate at a temperature of approximately 25 degrees Celsius or below when depositing the silane precursor.

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18. The system of claim 1, wherein the post-treatment module includes an annealing chamber, a vacuum pump system, a mass flow controller, and at least one valve controlling a flow of gas into the annealing chamber, and wherein the instructions are executable to hold an atmosphere within the annealing chamber at a pressure of 5 between approximately 1 and 10 Torr via the vacuum pump and the valve.

19. The system of claim 1, wherein the post-treatment module includes a substrate elevator and a plurality of heating elements for batch substrate processing.

10 20. The system of claim 1, wherein the first silane-containing layer is a first adhesion promoter layer configured to chemically bond to an underlying silicon-containing layer.

15 21. The system of claim 1, wherein the second silane-containing layer is a hard mask layer.

22. The system of claim 1, wherein the second silane-containing layer is an etch stop layer.

20 23. The system of claim 1, wherein the second silane-containing layer is a second adhesion promoter layer configured to chemically bond to an overlying silicon-containing layer.

24. A system for depositing a composite polymer dielectric film on a substrate, the composite polymer dielectric film including a low dielectric constant polymer layer disposed between a first adhesion promoter layer and an overlayer, wherein the overlayer includes at least one layer selected from the group consisting of a second adhesion 5 promoter layer, an etch stop layer and a hard mask layer, wherein the first adhesion promoter layer includes reactive silane groups configured to chemically bond to a silicon-containing layer that is in contact with the adhesion promoter layer, the system comprising:

10 a process module for forming the low dielectric constant polymer layer, wherein the process module includes a deposition chamber and a substrate holder configured to hold and cool a substrate during a deposition process;

a monomer delivery system for delivering a gas-phase diradical monomer to the deposition chamber;

15 a post-treatment module for annealing the composite polymer dielectric film, wherein the post-treatment module includes a heat source for heating the substrate and processing gas delivery system for delivering a reducing gas to the post-treatment module;

20 a silane deposition module for depositing the first adhesion promoter layer and the overlayer, wherein the silane deposition module includes a silane deposition chamber and a silane delivery system for delivering a silane precursor to the silane deposition chamber; and

a transfer module disposed between the process module, the silane deposition module and the post-treatment module, wherein the transfer module includes a substrate transport mechanism for transferring a substrate between the process module and the post-treatment module.

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25. The system of claim 24, wherein the silane deposition module includes at least one of a UV light source, a heater and a plasma source to generate free radicals in the silane precursor.

10 26. The system of claim 24, wherein the silane deposition module includes a plurality of silane delivery systems for delivering a plurality of silane compounds to the silane deposition chamber.

27. The system of claim 24, wherein the substrate holder includes a cooling 15 mechanism configured to cool the substrate when the substrate is in the holder.

28. The system of claim 27, wherein the substrate holder is an electrostatic chuck configured to allow a pressure of 10 psi or less of helium to be held between the chuck and the substrate to aid in cooling the substrate.

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29. The system of claim 24, wherein the monomer delivery system includes a vessel configured to hold a precursor to the gas-phase diradical, and a reactor configured to generate the diradical from the precursor.

5 30. The system of claim 29, wherein the monomer delivery system includes a vapor flow controller disposed between the vessel and the reactor.

10 31. The system of claim 24, wherein the silane delivery system includes an inert gas supply, a mass flow controller, and a silane vessel for containing and heating a volume of a silane precursor.

32. The system of claim 24, wherein the post-treatment module includes a hot plate for heating the substrate during annealing.

15 33. The system of claim 24, further comprising a first load lock and a second load lock coupled to the transfer module, wherein the first load lock is configured to accept insertion of a substrate into the system, and wherein the second load lock is configured to permit removal of a substrate from the system.

34. A computer-readable storage medium containing instructions stored thereon, wherein the instructions are executable by a processor on a wafer processing system to direct the wafer processing system to perform a method of forming a composite dielectric film on a wafer, the composite dielectric film including an adhesion promoter 5 layer having a plurality of silane groups, and a low dielectric constant polymer layer disposed on the adhesion promoter layer and chemically bonded to the adhesion promoter layer, the method comprising:

depositing a silane material onto the wafer;  
exposing the silane material to a free-radical generating energy source to generate 10 free-radicals from vinyl, keto or alkyl halide functional groups on the silane material and to form the first adhesion promoter layer;  
depositing the low dielectric constant polymer layer on the adhesion promoter layer by exposing the wafer to a concentration of a gas phase free radical; and  
heating the adhesion promoter layer and the polymer dielectric in the presence of 15 hydrogen.

35. The storage medium of claim 34, wherein the instructions are executable to direct the wafer processing system to deposit the low dielectric constant polymer layer while the substrate is held at a temperature of between approximately -30 and -50 degrees 20 Celsius by a cooled substrate holder.

36. The method of claim 34, wherein the adhesion promoter layer is a first adhesion promoter layer, and wherein the instructions are executable to direct the wafer processing system to deposit a second adhesion promoter layer on low dielectric constant polymer layer before heating under hydrogen.

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37. The method of claim 36, wherein the instructions are executable to direct the wafer processing system to expose the second adhesion promoter layer to free-radical generating energy after depositing the second adhesion promoter layer.

10 38. The storage medium of claim 37, wherein the free-radical generating energy is UV light.

15 39. The storage medium of claim 34, wherein the silane material is selected from materials having a general formula of  $(RZ)_x\text{-Si-(W-T)}_y$ , wherein W is selected from the group consisting of  $-\text{O-}$ ,  $-\text{CH}_2-$ ,  $-(\text{CH}_2)_a\text{C=OO-}$ , and  $-(\text{CH}_2)_a\text{-OO=C-}$ ; wherein T is selected from the group consisting of  $-\text{CR=CR'R''}$ , an alkyl halide, and  $-\text{RC=O}$ ; wherein Z is selected from the group consisting of O and NR; wherein R, R' and R'' are an H, alkyl or aromatic group; wherein a is 0 or an integer; wherein x = 1, 2 or 3; wherein y = 1, 2 or 3; and wherein x + y = 4.

40. The method of claim 34, wherein the silane material is selected from materials having a general formula of  $H_xSi-(W-T)_y$ , wherein W is selected from the group consisting of -O-, -CH<sub>2</sub>-, -(CH<sub>2</sub>)<sub>a</sub>C=OO-, and -(CH<sub>2</sub>)<sub>a</sub>-OO=C-; wherein T is selected from the group consisting of -CR=CR'R'', an alkyl halide, and -RC=O; wherein R, R' and R'' are an H, alkyl or aromatic group; wherein a is 0 or an integer; wherein x = 1, 2 or 3; wherein y = 1, 2 or 3; and wherein x + y = 4.

41. The storage medium of claim 34, wherein the low dielectric constant polymer layer is formed from a polymer material having a dielectric constant of less than 10 2.6.

42. The storage medium of claim 41, wherein the low dielectric constant polymer layer is formed from a poly(paraxylylene) having a general formula of  $-(C(F_xH_{2-x})-(C_6F_yH_{4-y})-C(F_xH_{2-x})-)-$ , wherein x = 0, 1 or 2, and wherein y = 0, 1, 2, 3 or 4.

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43. The storage medium of claim 42, wherein the low dielectric constant polymer layer is formed from a poly(paraxylylene)-based material having a general structure of  $-(CF_2-(C_6H_4)-CF_2)-$ , and wherein the low dielectric constant polymer layer is deposited with an initial crystallinity of 20-50% in a  $\beta_2$  phase of the material.

44. The storage medium of claim 34, wherein the low dielectric constant polymer layer is formed from a monomer having a general formula of  $X'm\text{-}Ar(CZ'Z''Y')_n$ , wherein Ar is an aromatic group or a fluorine-substituted aromatic group, wherein  $Z'$  and  $Z''$  are selected from the group consisting of H, F and  $C_6H_5$ , wherein  $X'$  and  $Y'$  are leaving groups removable to generate free radicals, wherein  $m$  and  $n$  are each equal to zero or an integer, and wherein  $m + n$  is less than or equal to a total number of  $sp^2$  hybridized carbons on Ar available for substitution.

45. The storage medium of claim 34, wherein the substrate has a surface, and 10 wherein the instructions are executable to direct the wafer processing system to expose the substrate to ultraviolet radiation before depositing the silane material onto the substrate to remove water from the substrate surface.

46. The storage medium of claim 34, wherein the instructions are executable to 15 direct the wafer processing system to heat the adhesion promoter layer and the low dielectric constant polymer layer under a mixture of 3-10% hydrogen in an inert gas.

47. The storage medium of claim 34, wherein the instructions are executable to 20 direct the wafer processing system to heat the adhesion promoter layer and the low dielectric constant polymer layer under hydrogen for 0.5-10 minutes.

48. The storage medium of claim 34, wherein the instructions are executable to direct the wafer processing system to heat the adhesion promoter layer and the low dielectric constant polymer layer under hydrogen for 3-4 minutes.

5 49. The storage medium of claim 34, wherein the instructions are executable to direct the wafer processing system to heat the adhesion promoter layer and the low dielectric constant polymer layer under hydrogen to a temperature of 300-400 degrees Celsius.